

^{29}Si AND ^{13}C -NMR SPECTRA OF VINYL- AND ALLYLSILANES* **J. SCHRAML^a, V. CHVALOVSKÝ^a, M. MÄGI^b and E. LIPPMÄA^b^a Institute of Chemical Process Fundamentals,

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^{29}Si and ^{13}C -NMR chemical shifts in vinyl- and allylsilanes of the type $(\text{CH}_3)_{3-n}\text{X}_n\text{Si}(\text{CH}_2)_m \cdot \text{CH}=\text{CH}_2$ ($m = 0$ and 1 , $\text{X} = \text{Cl}$, C_2H_5 , $\text{OC}(\text{CH}_3)_3$ and $\text{OSi}(\text{CH}_3)_3$) are presented. The observed ^{13}C -NMR chemical shifts of olefinic carbons and ^{29}Si chemical shifts in substituted vinylsilanes are in agreement with the early interpretation of ^1H -NMR spectra and with other properties of these compounds. According to this interpretation π electrons of the vinyl group are delocalized toward the silicon atom, other substituents on the silicon influence this delocalization both by their inductive effects and their own ability to supply unshared electrons to the silicon.

In allylsilanes silicon is less shielded and olefinic carbons are more shielded than in vinylsilanes.

In the previous papers of this series¹⁻⁴ we studied compounds of the type *I* with fluo-



rine, amino, and phenyl groups as the substituent Y. In the present paper we turn our attention to the compounds having vinyl groups in the place of the substituent Y. There are many literature references (for their list see⁵) to ^1H -NMR studies of vinyl- and allylsilanes, ^{29}Si and ^{13}C -NMR spectra of some individual compounds have been also occasionally reported⁶⁻¹⁴, but no systematic study of these spectra has yet appeared.

Following the suggestion of Hobgood, Goldstein and Reddy¹⁵ that the deshielding of protons in vinyltrimethylsilane is caused by the so-called $(p-d)_\pi$ bonding between silicon and vinyl groups we were able¹⁶ to interpret ^1H -NMR spectra of vinylsilanes of the type *I* ($m = 0$, $\text{Y} = \text{CH}=\text{CH}_2$) with $\text{X} = \text{Cl}$, $\text{OC}(\text{CH}_3)_3$, $\text{OSi}(\text{CH}_3)_3$ and OC_2H_5 . The interpretation¹⁶ assumed inductive effect of the silicon atom and $(p-d)_\pi$ bonding between this atom and each of its substituents. A competition between the substituents in their demands for the empty silicon $3d$ orbitals and their different ability to occupy these orbitals explained fully the trends observed in ^1H -NMR spectra and in other properties.

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At present, hyperconjugation or $\sigma - \pi$ interaction is receiving increasing attention in interpretation of various properties of organosilicon compounds. It is beyond the scope of the present paper to compare numerous studies in which claims for dominant role of hyperconjugation were stated with those claiming the same for the silicon $3d$ orbitals (some recent studies of this type include refs¹⁷⁻²¹ and papers quoted therein). The most of the theoretical studies used CNDO type calculations. The lack of satisfactory parametrization makes deductions from such calculations of doubtful reliability^{20,21} and some of the deductions are not substantiated by *ab initio* calculations²¹. According to Horn and Murell²¹ the *ab initio* SCF calculations show that the importance of the d -orbitals depends on the size of the base used but for a satisfactory interpretation of spectroscopic properties it is necessary to provide for some functions in the basis of the silicon atom which interact strongly with the virtual π^* orbital in ethene²¹. Apparently a safe conclusion would be that in addition to the silicon inductive effects, $\sigma - \pi$ and $p - d$ interactions must be considered in interpreting the properties of alkenylsilanes. The $\sigma - \pi$ interaction is more and the $p - d$ interaction is less important for allyl than for vinyl silanes.

In many aspects the model based on hyperconjugation is equivalent to that based on $(p - d)_\pi$ bonding and it seems to be essentially a question of convenience in which of the terms a discussion is cast²². As one of our concerns in the present paper is to find if the earlier interpretation of ^1H -NMR spectra can account also for ^{29}Si and ^{13}C -NMR spectra we adhere to the earlier terminology. Such an approach is also justified by the inability of the current theory of chemical shifts to differentiate the shielding effects of π electron transfer into $3d$ or σ orbitals at silicon.

An interpretation analogous to that accepted for vinylsilanes¹⁶ was recently offered to account for ^{13}C and ^{11}B -NMR spectra of vinylhaloboranes²³ and other alkenylboranes²⁴.

EXPERIMENTAL

Preparations and other properties of the silanes were described earlier^{16,25-31}. The purity of the compounds was checked by gas-chromatography. All the spectra were measured on the same spectrometer and by the same technique as described previously⁴ (*i.e.* in CW mode in neat liquids using TMS external reference). Only ^{13}C NMR spectrum of vinyltrimethylsilane was measured independently also on a Bruker spectrometer HX 90 at 22.63 MHz in 90 and 50% C_6D_6 solutions.

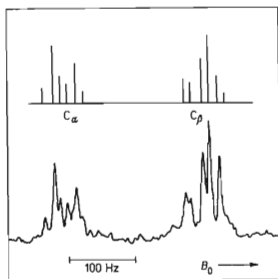


FIG. 1
Off Resonance ^1H Decoupled ^{13}C -NMR
Spectrum of Olefinic Carbons in Vinyltri-
methylsilane (lower trace is the actual re-
cording, upper trace is a schematic diagram)

Assignment of ^{29}Si lines in compounds containing two or more silicon atoms in the molecule was made on the basis of an observation that the shift of this nucleus in $(\text{CH}_3)_3^{29}\text{SiOSi}$ fragments is only very little affected by the substitution on the other silicon atom, the shift being in the range of 6.0–8.0 32 .

As the only ^{13}C -NMR data 9 on vinylsilanes that were available at the onset of this work showed the olefinic α carbon to be more shielded than the β carbon in vinyltrichlorosilane, our first results on vinyltrimethylsilane in which the order of olefinic carbon shielding was reversed appeared surprising. The uncoupled spectrum of vinyltrimethylsilane was of little help in as-

TABLE I
 ^{29}Si and ^{13}C -NMR Chemical Shifts in Vinylsilanes of the Type $(\text{CH}_3)_{3-n}\text{X}_n\text{SiCH}=\text{CH}_2^a$

Substituent X	n	Chemical shifts					
		$(\text{CH}_3)_{3-n}\text{Si CH}=\text{CH}_2$ group				Substituent X	
		$\delta(^{29}\text{Si})$	$\delta(^{13}\text{CH})$	$\delta(^{13}\text{CH}_2)$	$\delta(^{13}\text{CH}_3)$	$\delta(^{13}\text{CH}_3)$	Other
—	0	— 7.6	139.0 140.3 ^b	129.9 131.0 ^b	—2.2 —1.4 ^b	—	—
Cl	1	16.7	135.6	133.1	0.9	—	—
	2	16.5	134.0 135.2 ^c	137.3 138.0 ^c	5.7	—	—
	3	— 3.5	130.9 133.1 ^c 131.8 ^d 132.0 ^e	138.2 140.1 ^c 138.7 ^d 139.4 ^e	— — — —	— — — —	— — — —
$(\text{CH}_3)_3\text{SiO}$	1	— 4.8	139.4	131.0	0.3	1.8	$\delta(^{29}\text{Si}) = 7.4$
	2	—35.1	137.7	132.0	—0.2	2.1	$\delta(^{29}\text{Si}) = 7.5$
	3	—79.4	132.7	131.7	—	0.5	$\delta(^{29}\text{Si}) = 7.2$
$(\text{CH}_3)_3\text{CO}$	1	— 5.6	139.9	130.2	0.0	31.3	$\delta(^{13}\text{C}) = 71.3$
	2	—34.6	138.3	130.6	—0.3	31.1	$\delta(^{13}\text{C}) = 71.3$
	3	—59.2	134.0 ^f	134.0 ^f	—	31.2	$\delta(^{13}\text{C}) = 74.6$
$\text{CH}_3\text{CH}_2\text{O}$	1	2.7	137.1	131.4	—2.7	18.0	$\delta(^{13}\text{CH}_2) = 57.4$
	3	—60.3	129.5	134.7	—	17.6	$\delta(^{13}\text{CH}_2) = 57.6$
CH_3CH_2	1	— 4.4	138.8	131.4	—3.9	7.3	$\delta(^{13}\text{CH}_2) = 7.5$
	2	— 2.3	137.0	131.5	—6.5	7.2	$\delta(^{13}\text{CH}_2) = 5.4$
	3	— 1.7	135.2	131.3	—	6.5	$\delta(^{13}\text{CH}_2) = 2.6$
F	2	—13.4 ^g	128.8 ^h	137.6	—6.7 ⁱ	—	—

^a Chemical shifts in δ -scale (*i.e.* ppm units positive values indicate deshielding relative to TMS external), maximum error ± 0.3 ppm, unless otherwise noted values obtained in this study are given; ^b measured in 90% C_6D_6 solution; ^c value of ref. 13 , measured in $\text{C}_6\text{D}_{12} \pm 1$ ppm; ^d value converted from ref. 9 using $^{33}\delta(\text{C}_6\text{H}_6) = 128.7$, measured in neat liquid, ± 0.8 ppm; ^e value converted from ref. 12 using $^{33}\delta(\text{CS}_2) = 193.7$ measured in neat liquid ± 0.2 ppm; ^f overlapping lines; ^g $^1J(^{29}\text{Si}-^{19}\text{F}) = 285 \pm 2$ Hz; ^h $^2J(^{13}\text{C}-^{19}\text{F}) = 20 \pm 1$ Hz; ⁱ $^2J(^{13}\text{C}-^{19}\text{F}) = 16.5 \pm 1$ Hz.

signing the lines since the lines overlapped and were broadened due to the long range couplings to the methyl protons. Using off-resonance decoupling did not lead to usual simplification of the spectrum because of large geminal couplings ($^2J(^1\text{H}-\text{C}-^{13}\text{C})$). Nevertheless, as it is clear from Fig. 1, the off-resonance spectrum solves the problem of assignment, the low-field group of lines consists of a large doublet of smaller triplets (which are assigned to the α -carbon) and the high-field group consists of a large triplet of small doublets (which are assigned to the β carbon). When these measurements were complemented by the measurements of other vinylsilanes, the observed trends in ^{13}C shielding confirmed the above assignment of the lines in vinyltrimethylsilane.

Comparison of our results with literature data showed that in all cases (Tables I and II) that were available our values were by 1–3 ppm more diamagnetic. This could well be a systematic error in our measurements which would be due to the external referencing.

RESULTS AND DISCUSSION

^{29}Si and ^{13}C -NMR chemical shifts in vinyl- and allylsilanes are summarized in Tables I and II and the trends in series of derivatives are illustrated in Figs 2–4.

Carbon Chemical Shifts

Olefinic carbons. Unlike the vinylic protons which are all shielded less in substituted vinylsilanes than in model carbon compounds¹⁶, in ^{13}C -NMR only the β (terminal) olefinic carbons are shielded in vinylsilanes less than in 3,3-dimethyl-1-butene (in which olefinic α carbon occurs at $\delta = 149.0^{12}$ or $\delta = 149.7^{34}$ and β carbon at $\delta = 109.0^{12}$ or $\delta = 109.8^{34}$). At first, this difference in behaviour might appear as contradicting the interpretation of ^1H -NMR results mentioned in introduction. Miyajima and coworkers¹² have, however, shown that α carbon chemical shift is controlled by σ electron density (or by the inductive effect of the substituent and

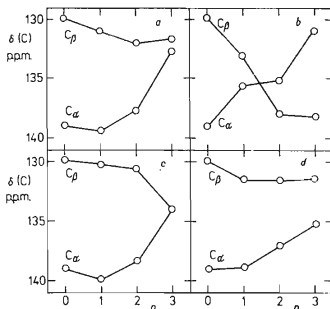


FIG. 2
 ^{13}C -NMR Chemical Shift Dependence of Olefinic Carbons on the Nature and Number n of Substituents X in Vinylsilanes of the Type I ($m = 0$), a $X = \text{OSi}(\text{CH}_3)_3$, b $X = \text{Cl}$, c $X = \text{OC}(\text{CH}_3)_3$, d $X = \text{CH}_2\text{CH}_3$

TABLE II
 ^{29}Si and ^{13}C -NMR Chemical Shifts in Allylsilanes of the Type $(\text{CH}_3)_3\text{-}_n\text{X}_n\text{SiCH}_2\text{CH}=\text{CH}_2^a$

Substituent X	n	Chemical shifts						
		$\delta(^{29}\text{Si})$	$\delta(^{13}\text{C})$	$\delta(^{13}\text{CH})$	$\delta(=\text{C}^{\text{13}}\text{CH}_2)$	$\delta(^{13}\text{CH}_3)$	$\delta(^{13}\text{CH}_3)$	Substituent X
—	0	24.4	133.8	112.1	—2.4	—	—	Other
		25.4 ^b	135.3 ^b	113.5 ^b	—1.5 ^b	—	—	
Cl	1	26.5	131.9	115.1	0.9	—	—	—
		38.3 ^b	133.0 ^b	116.3 ^b	2.4 ^b	—	—	
		27.7	128.5	116.7	3.3	—	—	
2	2	26.8	128.5	116.7	3.3	—	—	—
		29.6 ^b	130.6 ^b	118.9 ^b	5.2 ^b	—	—	
		30.7	127.1	119.4	—	—	—	
3	3	8.0	127.1	119.4	—	—	—	—
		31.6 ^b	128.1 ^b	120.6 ^b	—	—	—	
		26.8	134.2	113.7	0.1	2.1	$\delta(^{29}\text{Si}) = 7.3$	
$(\text{CH}_3)_3\text{SiO}$	1	4.1	134.2	113.7	0.1	2.1	$\delta(^{29}\text{Si}) = 7.3$	—
		—26.5	134.0	114.1	—0.6	2.1	$\delta(^{29}\text{Si}) = 6.9$	
		—70.3	133.7	114.1	—	1.8	$\delta(^{29}\text{Si}) = 7.3$	
$\text{CH}_3\text{CH}_2\text{O}$	3	—51.6	132.8	113.7	—	58.0	$\delta(^{13}\text{CH}_2) = 17.8$	—
		18.1	132.8	113.7	—	—	—	
		23.1	134.6	113.6	—3.8	—	—	
$\text{CH}_2 : \text{CHCH}_2$	1	0.2	134.6	113.6	—3.8	—	—	—
		21.5 ^b	134.8 ^b	114.4 ^b	—5.7 ^b	—	—	
$(\text{CH}_3)_3\text{SiCH}_2^c$	2	21.5 ^b	134.8 ^b	114.4 ^b	—5.7 ^b	—	—	—
		28.1 ^d	140.4	112.2	—1.8	—	—	

^a Chemical shifts in δ -scale, maximum error ± 0.3 ppm., unless otherwise noted values obtained in this study are given; ^b values of ref.¹¹ ± 0.2 ppm.; ^c compound of different type than in Table head. The compound has the structure $(\text{CH}_3)_3\text{SiCH}_2\text{CH}=\text{CH}_2$; ^d the value refers to allylic CH_2 group, $\delta(\text{Si}^{\text{13}}\text{CH}_2) = 15.8$.

in vinyl ethers was attributed to a conjugative transfer of electron density to the β carbon from the oxygen³⁵⁻³⁷ but the ^{13}C chemical shifts in vinyl sulphides³⁶ are consistent with electron displacement onto the vacant orbitals of sulphur³⁶.

Similarly as the range of vinylic proton chemical shifts decreases with increasing n in the compounds of the type $(\text{CH}_3)_{3-n}\text{X}_n\text{SiCH}=\text{CH}_2$, the chemical shift of the β carbon decreases and that of the α carbon increases with increasing n so that the two shifts get closer with increasing n (in the case of $\text{X} < \text{Cl}$ the two dependences even cross), see Fig. 2. Such a trend is in agreement with the observation of Yonemoto³⁴ who reported that in allyl compounds, $\text{R}-\text{C}_\alpha\text{H}_2-\text{C}_\beta\text{H}=\text{C}_\gamma\text{H}_2$, electronegative substituents R cause high field shift in $\delta(\text{C}_\beta)$ and the opposite in $\delta(\text{C}_\gamma)$, the two shifts being linearly related to each other (Fig. 5). The substitution effects were interpreted in terms of the π bond polarization due to the electric field of the substituent group³⁴. The gross features of the trend in vinylsilanes can be interpreted analogously by the varying electronegativity of the $(\text{CH}_3)_{3-n}\text{X}_n\text{Si}$ group, but in order to explain the larger shift changes with the substitution of the methyl groups by chlorine atom (which is less electronegative) than by oxygenous groups (which are more electronegative) one has to invoke the idea of substituent competition and the concept of different $(p-d)_n$ bonding ability of the substituents similarly as it was necessary in the interpretation of the proton spectra of these compounds¹⁶ or of ^{13}C and ^{11}B spectra of vinylboranes²³.

It was suggested³⁸ that the internal chemical shift, Δ , which is the difference between the shifts of the α and β carbon atoms can be taken as a measure of the polarity of the double bond $\text{C}=\text{C}$. Such a view is consistent with the Yonemoto³⁴ interpretation of the shifts in allyl compounds but as Miyajima and coworkers¹² showed, σ and π electron densities contribute differently to the observed internal shift. Nevertheless, if we take the internal shift in vinylsilanes for an approximate gross measure of the polarity of the vinyl group, then the observed internal shift in vinyltrimethylsilane indicates polarity in the sense $-\delta^+\text{CH}=\delta^-\text{CH}_2$. With increasing substitution of the silicon atom by electronegative groups the polarity decreases. The trend in allylsilanes is similar. In dichloro- and trichlorovinylsilane the polarity is reversed, *i.e.* $-\delta^-\text{CH}=\delta^+\text{CH}_2$. Such an interpretation is in agreement with the observed dipole moments³⁹ and with their interpretation.

The trend in the shielding in the series of vinylmethylethylsilanes demonstrates that some other factors also contribute to the observed shielding of vinylic carbon atoms. To attempt a full account of these minor features seems to us unpractical at this time though steric interactions (including inhibition of conjugation) is a likely candidate which explains the shifts in alkyl vinyl ethers and sulfides^{36,37}.

As it is apparent from Fig. 5 the chemical shifts of α and β carbons in vinylsilanes are linearly interrelated, but the regression line is, of course, different from that found for allyl compounds³⁴ (the points corresponding to allylsilanes studied here fall reasonably close to the Yonemoto regression line).

Maciel⁹ demonstrated rough linear relationships between the α carbon chemical shifts in vinyl derivatives and the corresponding shifts $\delta(\text{C-1})$ of the substituted carbon atom in phenyl compounds and between the β carbon shift and $\delta(\text{C-2})$ in the phenyl compounds. Such correlations hold also for the data reported here if they are plotted (Fig. 6) against the shifts in phenylsilanes studied earlier⁴, the regression lines have the same slopes as those of ref.⁹. The deviations apparent for the β carbon chemical shifts in compounds with SiCl_3 and $\text{Si}(\text{CH}_3)_2$ groups can be explained similarly as the deviations found for acetyl and carbethoxy substituents⁹. The negative charge that results from the electron withdrawal from β carbon atom can be distributed to two ortho carbons (as well as to the para position) in the phenyl compounds but in vinyl derivatives it must rest entirely on the β carbon atom.

In allylsilanes the two olefinic carbons are shielded similarly as the olefinic carbons in branched terminal alkenes⁴⁰. In agreement with our interpretation of olefinic carbon shielding in vinylsilanes and less pronounced delocalization in allylsilanes the terminal olefinic γ carbon atoms are shielded 10–18 p.p.m. more in substituted allylsilanes. It is surprising to see about equal sensitivity to the substituent effect in the two classes of compounds (compare Figs 2 and 3). The available data on allyl³⁴ and vinyl¹² compounds seem to support the common expectation of a stronger substituent effect in the compounds with shorter distance between the substituent

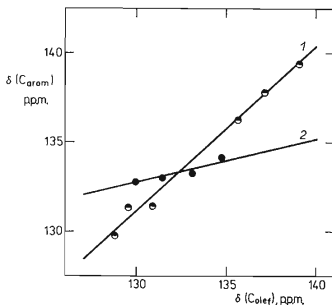


FIG. 5

Dependence of ^{13}C -NMR Chemical Shifts of Olefinic Carbons in CH_2 Groups, $\delta(^{13}\text{C}_{\text{olef}})$, on the Shifts of Olefinic Carbons in CH Groups, $\delta(^{13}\text{C}_{\text{arem}})$

The line 2 is taken from ref.³⁴, the points correspond to allylsilanes, the points of line 1 correspond to vinylsilanes.

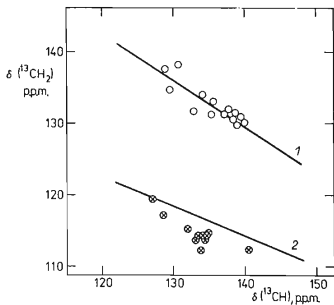


FIG. 6

Linear Correlations of Aromatic Carbon Chemical Shifts, $\delta\text{C}(\text{arem})$, in Phenylsilanes, 1 $\delta(\text{C-1})$ and 2 $\delta(\text{C-2})$, with Olefinic Carbon Chemical Shifts 1 $\delta(^{13}\text{CH})$ and 2 $\delta(^{13}\text{CH}_2)$ in Vinylsilanes

Data of ref.⁴ are taken for phenylsilanes.

and the carbon atom under consideration, but the picture is not completely clear. The β (olefinic) carbons in allylsilanes are shielded only 1–7 p.p.m. more than their counterparts in vinylsilanes.

Other carbons. 1) Allylic carbons. The pattern of variation of chemical shift $\delta(\text{Si}^{13}\text{CH}_2)$ with substitution (Table II) is similar to that of methyl carbons in methyl derivatives of the type $(\text{CH}_3)_{3-n}\text{X}_n\text{SiCH}_3$ (data taken from ref.⁴¹) but the substituent shifts are not equal in substituted methyl and allyl silanes as noted by Yonemoto³⁴ for other derivatives.

2) Methyl carbons. The chemical shift of the carbons of methyl groups bonded to the central silicon atom have almost the same values in corresponding vinyl and allyl silanes and they vary with the substitution on the silicon atom similarly as they do in other derivatives of silicon^{1-4,32,41,42}. Replacement of a methyl group in methylsilanes⁴¹ $(\text{CH}_3)_{3-n}\text{X}_n\text{Si}$ by a vinyl group increases the shielding of other methyl carbons, but this observation cannot be quoted in support of our interpretation since the effect of the same sign (and similar magnitude) is observed if the methyl group is replaced by an ethyl group⁴¹.

In vinyltri(tert-butoxy)- and vinyltriethylsilanes, where considerable crowding takes place, the tertiary and secondary carbons, resp., exhibit considerably different chemical shifts than in the corresponding mono- and di-derivatives.

Silicon Chemical Shifts. As it is apparent from the comparison of the trends shown in Fig. 4 with the trends reported for other derivatives^{1-4,6-8,32,41-43} the trend in the silicon shielding is not appreciably affected by the attached vinyl group but the silicon atom is shielded in all vinylsilanes by several p.p.m. more than in the corresponding allyl, ethyl, or methyl silanes. The factors contributing to the observed trends were discussed on several occasions (for a review see ref.⁴³). The increased shielding in vinylsilanes is in accord with our interpretation of olefinic carbon and proton chemical shifts discussed above. Similar increase in ¹¹B shielding was observed in vinylboranes in which analogous $(p-p)_\pi$ bonding is assumed²³. In contrast, ¹³C-NMR shifts of sp^3 carbons in alkenes (in which no back-bonding is considered) are affected by the alkene linkages similarly as they are affected by alkyl groups, providing conjugation is unimportant⁴⁴. In cases when the data for a comparison are available⁴¹ silicon is also more shielded in allylsilanes than in the corresponding ethyl- or propylsilanes. It is possible that this higher shielding is related to $\pi-d$ interaction which some authors assume also for allylsilanes.

The idea of substituent effects which has been widely used in ¹³C-NMR spectroscopy^{45,46} is also being used⁴³ in ²⁹Si-NMR. Two types of substituent chemical (SCS) shifts are frequently calculated. Firstly, the chemical shift in the substituted compound is compared with the shift in the compound in which the substituent is replaced by a hydrogen atom. For the compounds of the type I silicon SCF of the substituent Y, $\Delta\delta$, is defined as

$$\Delta\delta(\text{Si}) = \delta(\text{Si})[(\text{CH}_3)_{3-n}\text{X}_n\text{Si}(\text{CH}_2)_m\text{Y}] - \delta(\text{Si})[(\text{CH}_3)_{3-n}\text{X}_n\text{Si}(\text{CH}_2)_m\text{H}],$$

where $\delta(\text{Si})[\text{M}]$ denotes silicon-29 chemical shift in the compound M. Secondly, and often more conveniently, the shift is compared with the shift in the compound in which the substituent is replaced by a methyl group. Such SCS values are defined as follows

$$\bar{\Delta}\delta(\text{Si}) = \delta(\text{Si})[(\text{CH}_3)_{3-n}\text{X}_n\text{Si}(\text{CH}_2)_m\text{Y}] - \delta(\text{Si})[(\text{CH}_3)_{3-n}\text{X}_n\text{Si}(\text{CH}_2)_m\text{CH}_3].$$

For vinyl compounds only the SCS of the second kind is practical, for allyl compounds data are available only for the calculation of the SCS values of the first kind. The dependences of the SCS's on the nature and number of substituents on silicon atom are shown on Fig. 7. (Values given in refs^{32,41,47} were used in the evaluation of SCS). Comparison with similar dependences for other substituents^{1,2,43} is of only limited value since the SCS values for vinyl substituent reflect not only the addition of π electronic system but also a change in hybridization of the carbon atom attached directly to the silicon, while other substituents cause only second order rehybridization effects⁴⁸ on this carbon atom. Nevertheless SCS values of silicon for a number of combinations of substituents X and Y⁴³ are also negative and also their absolute value increases with increasing number n of electronegative substituents X as observed here. Similarly as in the case of other substituents Y, algebraic increase of negative values of SCS with n is caused by a polarization of Si—X bonds due to more electronegative vinyl than methyl groups.

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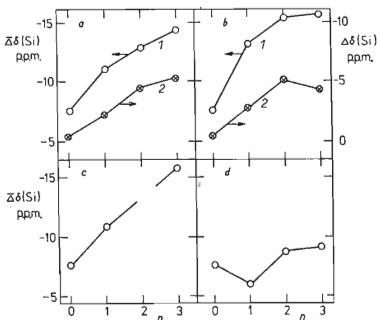


FIG. 7
Silicon Substituent Chemical Shifts, $\Delta\delta(\text{Si})$ and $\bar{\Delta}\delta(\text{Si})$ in Vinyl 1 and Allylsilanes 2 of the Type I ($m = 0$ and 1)

a X = OSi(CH₃)₃, b X = Cl, c X = OC₂H₅, d X = C₂H₅ (Data of refs^{32,41,47} were used).

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Note added in proof: M. Larin and V. Pestunovich (Irkutsk) have studied vinylsilanes of the type I with $X = C_6H_5$. Their results (private communication) are in agreement with the interpretation presented here.